Engineering Bulletin

⚫EPA

Supercritical Water Oxidation

Technology Status

Supercritical water oxidation (SCWO) has existed as an emerging waste treatment technology for approximately 10 years [1]. There are currently no full-scale SCWO systems in operation, but considerable bench- and pilot-scale data are available. The largest existing SCWO system can process waste at a rate of approximately 4 gallons per minute (gpm)[2].

Several universities and research institutes are studying SCWO. The U.S. Air Force is investigating SCWO for destruction of rocket fuels and explosives. The U.S. Department of Energy is considering SCWO for treatment of wastes generated at its nuclear plants [3]. SCWO is also being considered by National Aeronautics and Space Administration (NASA) for waste treatment during extended space missions [4][5].

The Defense Advanced Research Projects Agency (DARPA) is also investigating SCWO. Ongoing work under a DARPA contract includes the design and construction of a mobile SCWO unit for the destruction of military wastes. General Atomics is the prime contractor for this project and the University of Texas (UT) Balcones Research Center and Eco Waste Technologies (EWT) are subcontractors [6].

EWT is currently developing a proprietary SCWO system which operates above ground (surface SCWO). Besides its involvement in the DARPA project, EWT is also designing a 5-gpm commercial demonstration unit for a small chemical manufacturing facility [6].

Modell Development Corporation (MODEC) is also developing a proprietary surface SCWO system. MODEC hopes to have a 5 dry ton/day pilot plant completed in 1992 and small commercial units available in 1993 [7].

MODAR, Inc. owns and operates the 4-gpm SCWO system mentioned previously [2]. MODAR conducts surface SCWO research and development in conjunction with its licensor, ABB Lummus Crest [8][9].

GeneSyst International is developing a proprietary SCWO system called a "Gravity Pressure Vessel" which is designed to operate below ground (subsurface SCWO) [10].

Vertech was involved in the development of subsurface SCWO reactors, but it was purchased by Wijnanin N.V., which has Air Products and Chemicals as its U.S. licensee. It is not clear whether Wijnanin N.V. or Air Products and Chemicals plans to pursue SCWO development.

Oxidyne (previously Vertox) was also involved in subsurface SCWO development. Oxidyne developed plans for a full-scale, subsurface subcritical water oxidation reactor in Houston, Texas at Sims Bayou Sewage Treatment Plant. Construction of the reactor was initiated but was not completed due to insufficient funding [11][12][13]. Oxidyne is no longer involved in SCWO research and therefore sold a number of its patents and designs to City Management Corporation (CMC). CMC has no immediate plans to continue SCWO research [14]. The Oxidyne work in Houston is important because the design of that subcritical system may serve as a basis for the design of subsurface systems which operate at supercritical conditions.

Research currently being conducted by various firms and universities focuses on a better understanding of the SCWO process and will be used in the design of full-scale systems. Specific research topics include kinetics, the mechanisms of SCWO, and fluid flow characteristics [15][16].

Technology Description

In SCWO, decomposition occurs in the aqueous phase above the critical point of water (374°C/221 atmospheres or atm). A schematic of a generic SCWO process is provided in Figure 1. As shown in this figure, the feed stream is typically an aqueous waste. An oxidant such as air, oxygen, or hydrogen peroxide must be provided unless the waste itself is an oxidant.

A supplemental fuel source should also be available. Because oxidation is exothermic, SCWO is self-sustaining for a waste stream with an adequate chemical oxygen demand (COD). According to developers, SCWO is self-sustaining provided the waste stream has a COD of approximately 15,000 mg/L or higher [15]. Theoretically, SCWO may be self-sustaining for CODs as low as 5,000 mg/L [10]. At startup and for dilute wastes that will not autogenically sustain combustion, a supplemental fuel such as waste oil is added [17]. Alternatively, some

* [reference number]

Figure 1
SCWO Schematic

Figure 1
SCWO Schematic
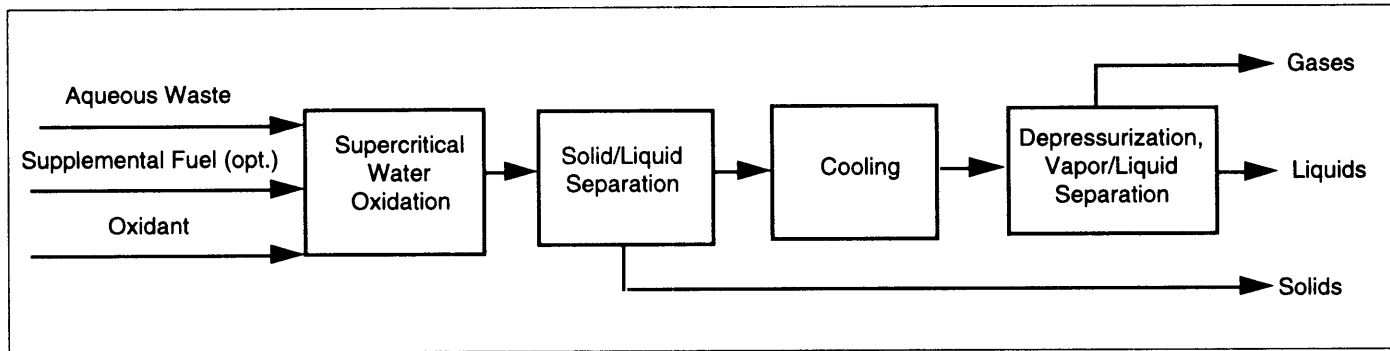
dilute wastes can be dewatered until they are concentrated enough to sustain SCWO without supplemental fuel [18]. Concentrated wastes, on the other hand, must be diluted if the oxidation of the waste will generate more heat than can be readily removed from the SCWO processing vessel [18].

The streams entering an SCWO reactor must be heated and pressurized to supercritical conditions. Influent streams are frequently heated by thermal contact with the hot effluent. Both influent pressure and backpressure (often a restriction of the outlet) must be provided. The influent streams are then combined at supercritical conditions and oxidation occurs.

Certain properties of supercritical water make it an excellent medium for oxidation. Many of the properties of water change drastically near its critical point: the hydrogen bonds disappear and water becomes similar to a moderately polar solvent; oxygen and almost all hydrocarbons become completely miscible in water; mass transfer occurs almost instantaneously; and the solubility of inorganic salts drops to the parts per million (ppm) range [19]. Because inorganic salts (as well as certain other solids) are nearly insoluble in supercritical water, solids removal must be considered in the design of a SCWO reactor [7][20][21].

The liquid effluent from SCWO is cooled (often by heat exchange with the influent) and returned to ambient pressure. As the effluent is cooled and depressurized, compounds such as carbon dioxide and oxygen will vaporize. According to SCWO developers, the effluent contains relatively innocuous products. Organic materials produce carbon dioxide and water; additional products depend upon the components of the waste. Nitrogen compounds principally produce ammonia and nitrogen as well as small amounts of nitrogen oxides (NO_x); halogens produce the corresponding halogen acids; phosphorus produces phosphoric acid; and sulfur produces sulfuric acid [18].

Vendors are currently developing both surface and subsurface SCWO systems. Figure 2 is a schematic of a subsurface SCWO reactor. As shown in Figure 2, subsurface SCWO reactors will consist of columns of aqueous waste which are deep enough that the material near the bottom is subjected to a pressure of at least 221 atm [22]. To achieve this pressure solely through hydrostatic head, a water column depth of approxi-

mately 12,000 feet will be required [10]. The influent and effluent will flow in opposite directions in concentric vertical tubes [13]. In surface SCWO systems, the majority of the pressure is provided by a source other than gravity, and the reactor is on or above the earth's surface.

Applicability

Surface and subsurface SCWO systems may have slightly different applications. Because subsurface SCWO systems are below ground, developers claim that the earth will provide protection in the event of a catastrophic reactor failure. Subsurface designs have additional advantages over surface SCWO systems, including fewer mechanical parts (which should lead to lower maintenance) and pressure provided by hydrostatic head [13].

Figure 2
Subsurface SCWO Reactor
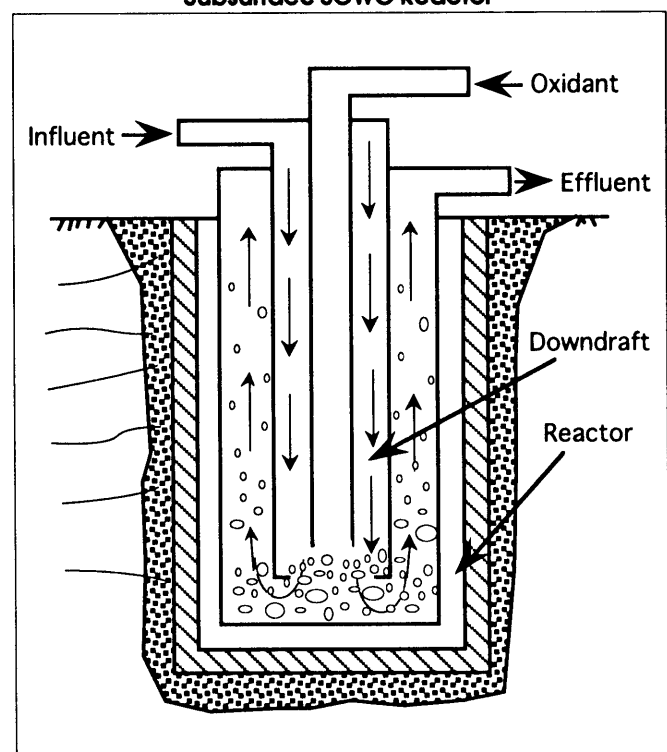
Surface SCWO systems, however, have several advantages over subsurface systems. Surface systems are much more accessible (and therefore easier to monitor) than subsurface reactors [13]. Developers project that it will not be cost-effective to construct subsurface reactors for small waste streams, as the drilling cost for the well is significant [10].

In general, applications of SCWO processes may include liquid wastes, sludges [13], and slurried solid wastes [18]. Potentially treatable compounds include halogenated and nonhalogenated aliphatic and aromatic hydrocarbons; aldehydes; ketones; esters; carbohydrates; organic nitrogen compounds; polychlorinated biphenyls (PCBs), phenols, and benzenes; aliphatic and aromatic alcohols; pathogens and viruses; mercaptans, sulfides, and other sulfur-containing compounds; dioxins and furans; leachable metals; and propellant components [12][13][18][22][23]. SCWO has been applied to municipal and industrial sludges. Tests performed on pulp mill sludges, for example, showed that SCWO can effectively treat these wastes (a total organic carbon destruction efficiency of 99.3 percent was achieved). Further analysis indicated that treatment of pulp mill sludges by SCWO should be able to compete economically with incineration and, in some regions, with landfilling [7].

SCWO also compares favorably with wet air oxidation (WAO), a commercially available technology which is similar to SCWO. In WAO, thermal decomposition and hydrolysis occur as well as oxidation. WAO is conducted in the aqueous phase and typically utilizes temperatures ranging from 150 to 300°C and pressures up to 200 atm. SCWO provides a number of advantages over WAO, including higher destruction efficiencies (DEs) and lower reaction times [24]. SCWO is also more energy-efficient than WAO [25].

The minimum waste concentration for which SCWO is applicable is waste-specific and can be determined by a cost comparison. The costs associated with dewatering the waste, operating the SCWO system, and purchasing supplemental fuel must be considered. There is also a maximum waste concentration for which SCWO is applicable because the oxidation of the waste must not generate more heat than can be readily removed from the processing vessel [18]. Note, however, that wastes which exceed the maximum concentration can be diluted prior to SCWO. MODAR literature states that its SCWO process is most applicable to wastes with hydrocarbon concentrations of 1 to 30 percent but it does not specify the concentrations of the wastes fed to the SCWO reactor [21].

SCWO developers claim several advantages associated with SCWO as a means of destroying wastes:

* One vendor plans to design a SCWO system which will be transportable and thus applicable to Superfund sites [6].
* One developer claims that the SCWO process is odor-free and extremely quiet [11].
* According to developers, SCWO reactions are self-sustaining provided the waste stream has a COD of approximately 5,000 mg/L or higher [10]. By contrast, self-sustaining incineration requires a minimum

COD of approximately 300,000 mg/L [15].
* Because SCWO systems operate in a lower temperature range (400 to 600°C) than typical incineration systems, researchers believe that SCWO will produce lower quantities of NO_x [26].

Developers claim that SCWO is relatively safe because the reaction temperature can be controlled through adjustment of the degree of preheating and/or the concentration of the waste [7]. The high temperatures and pressures necessary for SCWO are potentially dangerous, but designing SCWO reactors with large safety factors should reduce the risk. One developer indicates the failure of a heater tube at approximately 3700 psi and 1400°F produced a loud pop and damage to local insulation, but no injuries and no damage to adjacent equipment or instrumentation. The developer further states that fluid loss from the rupture was minimal [6].

A second danger involves the possibility that the process could be interrupted, causing an incomplete reaction which could produce dangerous offgases. SCWO systems can be designed to provide an emergency shutdown option and it is known that at least one pilot-scale system includes such a provision [6]. Note that the above are only potential dangers, as no safety problems were documented in the literature reviewed.

Limitations

The density of water drops rapidly between 300 and 400°C, and SCWO systems typically operate at or above 400°C. The low densities associated with the supercritical temperatures can result in the deposition of salts and pyrolytic chars. Deposition may result in plugging problems or added cleaning requirements. Some researchers prefer near-critical water oxidation at approximately 300°C, as the density of water is higher and salts and chars are more likely to remain dissolved [27]. Other developers prefer SCWO and are researching solutions to the deposition problem.

Possible problems due to corrosion must be examined when SCWO is considered. Several studies have been conducted regarding the minimization of corrosion in SCWO systems. Titanium, stainless steel 316, Hastelloy C-276, and Monel 400 were considered as alternative materials of construction for SCWO reactors. The results of these studies indicated that titanium had excellent corrosion resistance but its structural properties were unsatisfactory. Stainless steel 316 exhibited adequate corrosion resistance for use at low supercritical temperatures and moderate pH levels and chloride concentrations; a hastelloy (or another nickel-chrome alloy) is recommended for more corrosive conditions (low pH levels or high chloride concentrations). The monel had poor corrosion resistance and is therefore not recommended for SCWO reactor construction [25]. The use of ceramics and ceramic coatings in conjunction with the above metals has also been proposed [10].

High-temperature flames which have been observed during SCWO may present an additional equipment problem in both surface and subsurface SCWO systems. Research is being

conducted to determine what factors influence these "hydrothermal" flames because there is some concern that these flames will cause "hot spots" which could weaken SCWO vessels [1].

Other drawbacks associated with SCWO (as well as other oxidation technologies) include the slow oxidation rate of many polyhalogenated hydrocarbons and the production of dioxins from the oxidation of certain halogenated organics [27]. The production of dioxins may not present a significant problem, however, as the destruction of dioxins by SCWO has been documented [7].

Acetic acid is generally considered one of the most refractory byproducts of the SCWO of industrial wastes [28]. The acetic acid DEs shown in Table 1 reflect a portion of the performance data collected on this compound.

Ammonia, a second refractory compound, is produced by water oxidation of nitrogen-containing wastes at temperatures of 300 to 400°C [19]. Water oxidation does not degrade ammonia at any significant rate at these temperatures. If a water oxidation system is to be operated at or below 400°C, the ammonia may be removed by steam stripping or some other method. Above 425°C, organic nitrogen and ammonia in an SCWO system will decompose at a significant rate [19]. The primary products of this decomposition (below 650°C) are N_2 and N_2O, which further decompose to form N_2 and O_2 [12].

Table 1
SCWO Performance Data

Pollutant	Temp. (deg. C)	Pressure (atm.)	DE (%)	React Time (min.)	Oxidant	Ref.	Feed Conc. (mg/L)
1,1,1 - Trichloroethane	495		99.99	4	Oxygen	13	
1,1,2,2 - Tetrachloroethylene	495		99.99	4	Oxygen	13	
1,2 - Ethylene dichloride	495		99.99	4	Oxygen	13	
2,4 - Dichlorophenol	400		33.7	2	Oxygen	13	2,000
2,4 - Dichlorophenol	400		99.440	1	H_2O_2	13	2,000
2,4 - Dichlorophenol	450		63.3	2	Oxygen	28	2,000
2,4 - Dichlorophenol	450		99.950	1	H_2O_2	28	2,000
2,4 - Dichlorophenol	500		78.2	2	Oxygen	28	2,000
2,4 - Dichlorophenol	500		>99.995	1	H_2O_2	28	2,000
2,4 - Dimethylphenol	580	443	>99	10	$H_2O_2+O_2$	29	135
2,4 - Dinitrotoluene	410	443	83	3	Oxygen	29	84
2,4 - Dinitrotoluene	528	287	>99	3	Oxygen	29	180
2 - Nitrophenol	515	443	90	10	Oxygen	29	104
2 - Nitrophenol	530	430	>99	15	$H_2O_2+O_2$	29	104
Acetic acid	400		3.10	5	Oxygen	13	2,000
Acetic acid	400		61.8	5	H_2O_2	13	2,000
Acetic acid	450		34.3	5	Oxygen	28	2,000
Acetic acid	450		92.0	5	H_2O_2	28	2,000
Acetic acid	500		47.4	5	Oxygen	28	2,000
Acetic acid	500		90.9	5	H_2O_2	28	2,000
Activated sludge (COD)	400	272	90.1	2		30	62,000
Activated sludge (COD)	400	306	94.1	15		30	62,000
Ammonium perchlorate	500	374	99.85	0.2	None	18	12,000
Biphenyl	450		99.97	7	Oxygen	13	
Cyclohexane	445		99.97	7	Oxygen	13	
DDT	505		99.997	4	Oxygen	13	
Dextrose	440		99.6	7	Oxygen	13	
Industrial sludge (TCOD)	425		>99.8	20	Oxygen	19	
Methyl ethyl ketone	505		99.993	4	Oxygen	13	
Nitromethane	400	374	84	3	None	18	10,000
Nitromethane	500	374	>99	0.5	None	18	10,000
Nitromethane	580	374	>99	0.2	None	18	10,000
o - Chlorotoluene	495		99.99	4	Oxygen	13	
o - Xylene	495		99.93	4	Oxygen	13	
PCB 1234	510		99.99	4	Oxygen	13	
PCB 1254	510		99.99	4	Oxygen	13	
Phenol	490	389	92	1	Oxygen	29	1,650
Phenol	535	416	>99	10	Oxygen	29	150

Performance Data

Significant bench- and pilot-scale SCWO performance data are available. Typical DEs for a number of compounds are summarized in Table 1. Although several low DEs are included in this table to illustrate the fact that DE is proportional to both temperature and residence time, DEs in excess of 99 percent can be achieved for nearly all the pollutants studied.

Studies have been conducted to examine the effects of various parameters on SCWO DEs. The operating parameters studied include temperature, residence time, pressure, feed concentration, amount of oxidant (as a multiple of stoichiometric requirements), and type of oxidant [13][16][28].

As noted above, DE was found to increase with operating temperature and residence time. DE also increases with operating pressure, but only slightly [28]. Recent studies also indicate that the addition of catalysts such as potassium permanganate, manganous sulfate, copper, and iron can enhance DEs [13].

In at least one study, DE was found to increase slightly with feed concentration. The relationship between DE and amount of excess oxidant provided has also been examined. DE increases with increasing amounts of oxidant from 100 to 300 percent of the stoichiometric requirements; adding over 300 percent of the stoichiometric amount of oxidant does not significantly affect DEs [16][28].

Early SCWO systems used either oxygen or air as oxidants. Bench-scale studies were conducted to compare the DEs resulting from the use of air and oxygen, but no statistical difference was found [13]. In 1987, Welch and Siegwarth developed and patented a variation of SCWO which uses hydrogen peroxide as the oxidant. In Welch and Siegwarth's system, liquid hydrogen peroxide is mixed with the influent wastewater or slurry [13].

Welch, Siegwarth, and other researchers have shown that the use of hydrogen peroxide as an oxidant in SCWO systems produced DEs which were significantly higher than those obtained from the use of air or oxygen for the compounds tested [13][28]. Oxidation with hydrogen peroxide and oxidation with oxygen or air proceed by different mechanisms. This difference may result in higher DEs for either hydrogen peroxide or oxygen depending on the particular organic compounds being degraded [28]. Several other factors may influence the choice between oxidants. Hydrogen peroxide is significantly more expensive than oxygen but aqueous hydrogen peroxide is easier to pump, requires a less expensive feed system, and may be combined with the influent more readily than oxygen [10][28].

Process Residuals

In general, residuals from SCWO processes include gases, liquids, and solids. The gaseous effluent from the bench-scale treatment of pulp mill sludges was found to primarily consist of oxygen and carbon dioxide, with small concentrations of nitro-

gen [7]. Gaseous effluent from the bench-scale treatment of propellant components was also analyzed and found to contain nitrous oxide (N_2O) and oxygen. Analysis by mass spectroscopy did not detect the presence of chlorine (Cl_2), nitrosyl chloride (NOCl), or nitrogen dioxide (NO_2). These are positive results because they indicate that SCWO avoided the hazardous products such as Cl_2 and NOCl formed in typical thermal decomposition. In addition, SCWO appears to produce relatively little NO_x [18].

The aqueous effluent from the SCWO of pulp mill sludge had a total organic concentration (TOC) of only 27 ppm. The major inorganics present were calcium, chlorine (as chloride ion), nitrogen (as ammonia), sodium, and sulfur (as sulfate). The minor elements identified were all present at concentrations below Environmental Protection Agency (EPA) groundwater pollution criteria [7]. Liquid effluent from the SCWO of propellant components contained sodium chloride (NaCl), nitrite, and nitrate. The developer believes that the majority of the chlorine from the propellant exists as NaCl, but a chlorine mass balance has not yet been attempted [18].

Limited data describing solid residue from SCWO are available. When a bench-scale SCWO system was used to treat pulp mill sludges, benzene and lead were the only pollutants which the toxicity characteristic leaching procedure (TCLP) detected at concentrations above EPA groundwater limits. Benzo(a) pyrene and PCB, however, had detection limits above the groundwater limit. Based on these results, the developer believes that the solid residue from SCWO should easily qualify for disposal in any sanitary landfill [7]. Before disposal in a sanitary landfill will be allowed, however, the residue must be delisted.

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Acknowledgments

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